Polyhedron 108 (2016) 59–66

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Principles of precursor design for vapour deposition methods

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ARTICLE INFO

Article history:
Received 6 June 2015
Accepted 24 August 2015
Available online 2 September 2015

Keywords:
Atomic layer deposition
Chemical vapour deposition
Precursor design
Thermogravimetric analysis
Synthesis

ABSTRACT

Chemical vapour deposition (CVD) and atomic layer deposition (ALD) are attractive techniques for depositing a wide spectrum of thin solid film materials, for a broad spectrum of industrial applications. These techniques rely on volatile, reactive, and thermally stable molecular precursors to transport and deposit growth materials in a kinetically controlled manner, resulting in uniform, conformal, high purity films. Developments in these fields depend on careful precursor design. We discuss the qualities that make successful CVD or ALD precursors (low melting point, high volatility, stability and specific reactivity) and the widely applicable design principles used to achieve them, through examples of group 11 and 13 precursors including amidinates, guanidinates and iminopyrrolidinates. We highlight the most valuable techniques that we use to asses potential precursors on the basis of the discussed qualities, and to elucidate relevant mechanisms of decomposition and surface reactivity. There is a strong focus on thermogravimetric analysis (TGA), and solid state (SS) and solution NMR studies.

1. Introduction

Chemical vapour deposition (CVD) and atomic layer deposition (ALD) technologies are increasingly regarded as critical fields of study [1–3]. These versatile gas-phase thin film deposition techniques have made possible the deposition of a diverse array of solid materials. These include pure elements, oxides, nitrides, sulfides, and other more complex materials (e.g. ternary or doped), covering the majority of the periodic table [4]. This versatility combined with high quality deposited films leads to many applications spanning a number of industrial and academic interests. There is a strong focus on thin film deposition in the microelectronics industry, which requires conducting, insulating, and semiconducting layers with high purity and structural quality [5]. Excellent uniformity and conformality over high aspect ratio features can be achieved, particularly with ALD, which is increasingly important in this sector. Other industrial applications include corrosion and wear resistant coatings, diffusion barrier layers, photovoltaic layers, reflective and transmissive coating, light filters, catalyst coatings for porous materials, and hydrophilic or hydrophobic coatings [6].

Both CVD and ALD employ one or more volatile molecular precursors which are entrained to a substrate where they thermally react to deposit a thin solid film. These similar techniques differ in the nature of the precursors' reactivity. In contrast to CVD, which is a continuous growth process, ALD is characterised by controlled, stepwise growth, enabling Ångström-scale control over film thickness, and nanometric control over composition [7]. This is achieved by separating the film growth mechanism into independent, self-limiting half-reactions, each involving only one of at least two participating precursors. A typical ALD cycle involves four steps:

1. Precursor A is pulsed into the reactor, where it chemisorbs onto the existing film surface producing no more than one monolayer of a stable surface species, and volatile by-products. Excess precursor is unreactive with the surface it has formed.
2. The reactor is purged with inert gas to remove all unreacted precursor. This step is necessary to prevent the direct reaction of precursors A and B, which would result in uncontrolled CVD growth.
3. Precursor B reacts with monolayer A in a self-limiting fashion (i.e. to form a single monolayer of target film). The initial surface is regenerated, with which precursor A can react in the next cycle.
4. Inert gas purge.

This cycle is repeated to build up a film in a layer-by-layer fashion. For multi-component films, each precursor typically delivers only one of the film's components. In the case of metal deposition, typically one precursor contains the metal centre, while the other (referred to as the secondary precursor) serves to remove any

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http://dx.doi.org/10.1016/j.poly.2015.08.024
0277-5387/

remnants of the ligand system contained in the surface species, with the simultaneous reduction of the metal centre.

Precursor design is central to the advancement of CVD and ALD technologies, which focuses on accessing new materials, and improving film quality and process scalability. These techniques rely on the chemistry at the surface of the growing film, and therefore the chemical behaviour of the precursor is of paramount importance. Although the ALD deposition process is apparently simple, achieving this simplicity imposes demanding requirements on a precursor's physical and chemical properties. Similar, although slightly less demanding, requirements apply to CVD precursors. Precursors must be sufficiently volatile and thermally stable to be transported to the substrate intact, yet they must be reactive with the surfaces of the substrate and growing film. In the case of ALD the precursor must react to form no more than one self-limiting monolayer. A low melting point is desirable as liquids deliver a more consistent vapour pressure, although this is not a strict requirement. These criteria provide useful guidelines in the early stages of assessing potential precursors.

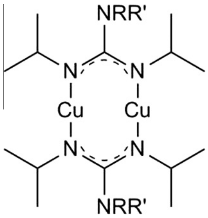
Our research focuses mainly on precursors containing group 11 and group 13 metal centres. Metallic Cu, Ag, and Au have low resistivities, and are useful as interconnect materials for microelectronic applications [8,9]. Furthermore, these materials have useful plasmonic properties for sensing applications. On the other hand, group 13 precursors are commonly used to deposit semiconducting or insulating binary extended solids [10]. For example, alumina is used as a dielectric gate oxide, corrosion resistant coating, and optical coating [5], while gallium oxide is a wide band gap (4.9 eV) semiconductor with plasmonic and optoelectronic applications [11,12]. Thus, our target film materials represent two common and very different classes of film materials, that rely on the precursors undergoing very different chemistry. We use these examples to illustrate that, despite the diversity of CVD and ALD processes, there are common themes among all precursors in terms of the design principles which relate structural features to targeted chemical and physical properties.

2. Melting point

A low melting point is ideal for precursor compounds. Because the ALD process requires repeatable precursor dosing in each pulse to ensure that saturation is achieved without resorting to excessively long pulses, liquid precursor compounds are preferable in the interest of minimising precursor waste and processing time. Liquids produce a more constant vapour pressure than solids, for two reasons. Firstly, liquids maintain a constant surface area as precursor is depleted; the surface area impacts the kinetics of volatilisation, and for a solid precursor is dependent on particle size and thus can change unpredictably over time and will likely vary from batch to batch. Secondly, solids have a tendency to concentrate impurities at their surface during volatilisation, hindering volatility, where liquids (ideally) have a continually refreshed and constant surface composition. The best precursor melts between room temperature and the process temperature, so that it can be easily transported and stored as a solid but used as a liquid.

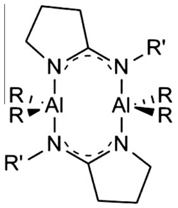
There are a number of strategies for tuning melting point which require only subtle alterations to the precursor structure. These are largely based on altering the entropy change of crystallization. Reducing the precursor's symmetry forces it to adopt a more specific conformation in the crystalline state, frustrating crystallization and thus lowering the melting point. This is exemplified by the copper guanidinate precursors **1** and **2**; by changing the R groups on the exocyclic amide moiety from two methyl groups to a proton and an *iso*-propyl, the melting point is lowered by 30 °C (Table 1) [13].

Table 1
Melting points of copper guanidinates [13].



Compound	R	R′	Melting point (°C)
1	Me	Me	109
2	H	^{i}Pr	79

Table 2
Melting points of aluminium dialkyl iminopyrrolidinates [14].



Compound	R	R′	Melting Point (°C)
3	Me	*N*-Propyl	79–83
4	Me	*iso*-Propyl	87–91
5	Me	*N*-Butyl	68–70
6	Me	*iso*-Butyl	111–113
7	Me	*sec*-Butyl	62–65
8	Me	*tert*-Butyl	116–118
9	Et	*iso*-Propyl	120–124
10	Et	*sec*-Butyl	60–63
11	Et	*tert*-Butyl	63–64

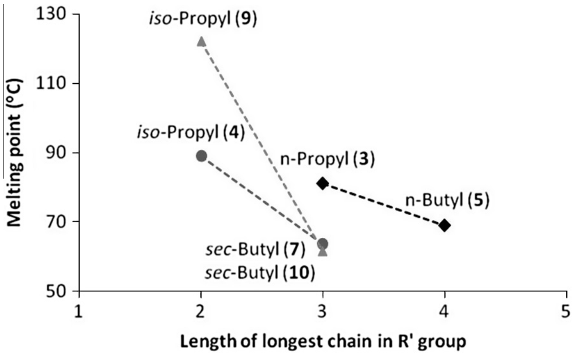


Fig. 1. Melting point as a function of chain length at constant number and position of branches in the R′ groups of the iminopyrrolidinates **3**, **4**, **5**, **7**, **9**, and **10**. Compounds with one branch, which is beta to the metal centre, in the R′ group are labelled with ● (R = Me) or ▲ (R = Et); compounds with unbranched R′ groups are labelled with ◆ (R = Me) [14].

A second common strategy for lowering the melting point is to include long, low-branched or unbranched alkyl chains. These become highly mobile in the liquid state, making melting more entropically favourable. Furthermore, long alkyl chains reduce intermolecular interactions in the compounds' crystalline lattice